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Phenyltetrafluorotelluromethoxide — a new fluorinating reagent for olefins

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Phenyltetrafluorotelluromethoxide fluorinates olefins to form 1,2-difluorides. The reaction with styrene afforded 1-fluoro-4-phenyl-1,2-dihydronaphthalene as the main product.

Key words: electrophilic addition, fluorination, olefins.

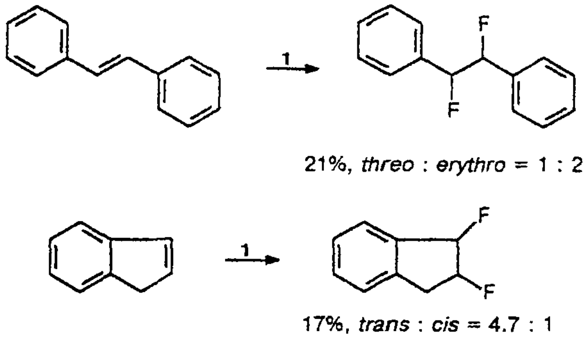
Phenylchalcogenopentafluorides are soft difluorinating reagents for olefins.[1] We found that, like the above-mentioned pentafluorides, *trans*-phenyltetrafluorotelluromethoxide (**1**) (which has been synthesized previously[2] by the reaction of an equimolar amount of trimethylsilyl methoxide with phenyltelluropentafluoride (Scheme 1)) is an electrophilic fluorinating reagent.

Scheme 1

1

The reactions of compound **1** with *trans*-stilbene and indene afforded the usual products of difluorination (Scheme 2).

Scheme 2



21%, *threo* : *erythro* = 1 : 2

17%, *trans* : *cis* = 4.7 : 1

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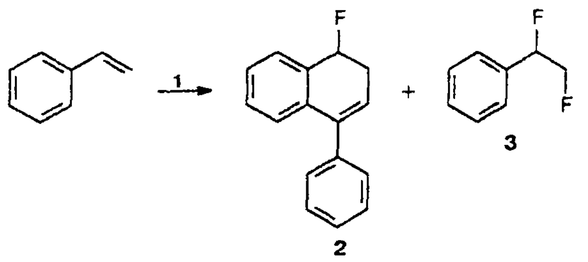
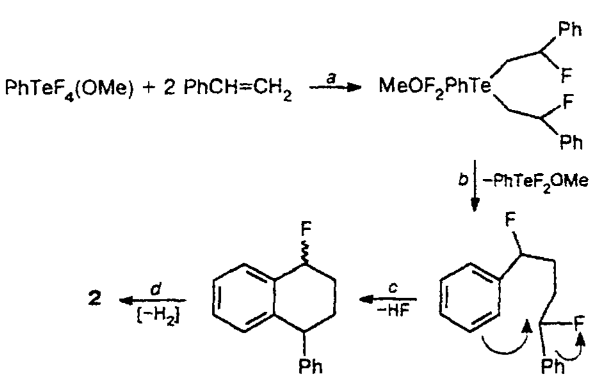
The reaction of **1** with styrene proceeded in a different manner (Scheme 3) to give 1-fluoro-4-phenyl-1,2-dihydronaphthalene (**2**) as the major product in addition to the expected 1,2-difluoride (**3**).

Scheme 3



The mechanism of formation of product **2** is not totally clear although it is evident that its molecule consists of two styrene molecules. We suggested a scheme (Scheme 4), which involves the following stages: (*a*) addition of two styrene molecules at the Te—F bonds, (*b*) oxidative coupling of two fluoroalkyl substituents at the hypervalent tellurium atom (the possibility of this coupling was considered in Ref. 3), (*c*) Friedel—Crafts intramolecular cyclization (the use of tellurium halides as catalysts was reported in Ref. 4), (*d*) oxidation of substituted tetralin to dihydronaphthalene **2** (apparently, high-valence compounds of Te served as oxidants; numerous examples of oxidative action of these compounds were reviewed, see Ref. 5).

Scheme 4



Experimental

The NMR spectra were recorded on a Bruker CXP-200 spectrometer. The yields of the reaction products were determined without isolation by the method of internal standard from the ^{19}F NMR spectral data (a precisely measured quantity of hexafluorobenzene or *m*-fluorotoluene was added to the reaction mixture, and joint integration of the reference signals and the signals of the products was carried out). The ratio of isomers was determined by integration. The ^1H and ^{13}C chemical shifts were measured relative to Me_4Si. The ^{19}F chemical shifts were measured relative to CF_3COOH. Positive values were assigned to low-field signals.

A solution of $(PhTe)_2$ (205 mg, 0.5 mmol) in CH_2Cl_2 (10 mL) was cooled to −95 °C, and XeF_2 (423 mg, 2.5 mmol) was added. After the solution became colorless, a solution of trimethylsilyl methoxide (104 mg, 1 mmol) in CH_2Cl_2 (3 mL) was added. The solution was allowed to warm to 0 °C, and a solution of styrene (104 mg, 1 mmol) in CH_2Cl_2 (3 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h. The solvent was distilled off, and the residue was extracted with ether. The extract was washed with a saturated solution of Na_2CO_3 and dried with $CaCl_2$. Column chromatography (SiO_2, hexane—CH_2Cl_2) gave product **2** (194 mg, 97%) as a viscous glassy compound. ^1H NMR (220 MHz, $CDCl_3$), δ: 6.2 (dd, H-3, $^3J_{H(3),H(2)} = 3.8-4.1$ Hz, $^3J_{H(3),H(2')} = 9.1-9.4$ Hz); 5.82 (ddd, H-1, $^2J_{H(1),F} = 48.5$ Hz, $^3J_{H(1),H(2)} = 9.68$ Hz, $^3J_{H(1),H(2')} = 3.1$ Hz); 2.86 (dddd, H-2, $^2J_{H(2),H} = 15$ Hz, $^3J_{H(2),F} = 11.8$ Hz); 2.65 (dddd, $^3J_{H,F} = 34$ Hz); 7.6 (d, 1 H arom., $^3J = 6.5$ Hz); 7.35—7.55 (m, 8 H arom). ^{13}C NMR (50.3 MHz, $CDCl_3$), δ: 125.3 (CH, C(8), $^3J_{C,F} = 6.8$ Hz); 90.9 (CH, C(1), $^1J_{C,F} = 172$ Hz); 69.1 (CH, C(3), $^3J_{C,F} =$ 4 Hz); 50.7 (CH, C(2), $^2J_{C,F} = 25$ Hz). ^{19}F NMR (188 MHz, $CDCl_3$), δ: −98.2 (ddd, $^2J_{H,F} = 48.5$ Hz, $^3J_{H,F} = 11.8$, 34 Hz). Mass spectrum (50 eV), *m/z* (I_{rel} (%)): 222 (27.5) $[M-2H]^+$, 206 (71.3) $[M-F+H]^+$, 205 (35.2) $[M-F]^+$, 204 (100) $[M-HF]^+$, 203 (64.0) $[M-H_2F]^+$, 202 (38.1), 187 (20.6).

The ^{19}F NMR spectrum of difluoride **3** corresponds to the published data[1,6]: −147.9 (tt, $^2J_{F,H} = 48$ Hz, $^3J_{F,H;H,H} =$ 32 Hz); −111 (m). The yield of **3** was 3% (NMR).

The reactions of **1** with *trans*-stilbene and indene were carried out analogously. The ^{19}F NMR spectra (δ) of the fluorination products correspond to the published data.[1] 1,2-Difluoro-1,2-diphenylethane, δ: −109.5 (AA′XX′, *erythro*); −105.5 (AA′XX′, *threo*). 1,2-Difluoroindane, δ: −99 (m); −110 (m, *trans*); −113 (m), −123 (m, *cis*).

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